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14. ABSTRACT This research addresses perceived needs of the U.S. Army in the development and use of biodiesel fuels and in the combustion chemistry of small cyclic nitramines. Studies are described of the chemistry of simple methyl and ethyl esters chosen as surrogates for the long chain mono-alkyl esters that are primary constituents of biodiesel fuels. The principal goal of these studies is the elucidation of the reaction mechanisms responsible for observed reductions in particulates, polycyclic aromatics, carbon monoxide, and unburned hydrocarbons when biodiesel is					
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Report Title

Quantitative Study of the Effects of Chemical Additives in Propellant Flames

ABSTRACT

This research addresses perceived needs of the U.S. Army in the development and use of biodiesel fuels and in the combustion chemistry of small cyclic nitramines. Studies are described of the chemistry of simple methyl and ethyl esters chosen as surrogates for the long chain mono-alkyl esters that are primary constituents of biodiesel fuels. The principal goal of these studies is the elucidation of the reaction mechanisms responsible for observed reductions in particulates, polycyclic aromatics, carbon monoxide, and unburned hydrocarbons when biodiesel is introduced as an additive to petroleum diesel. A recent research initiative is the study of the flame chemistry of morpholine, a simple cyclic nitramine, distantly related to the complex nitramine propellants HMX and RDX.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. C. K. Westbrook, W. J. Pitz, P. R. Westmoreland, F. L. Dryer, M. Chaos, P. Oßwald, K. Kohse-Höinghaus, T. A. Cool, J. Wang, B. Yang, N. Hansen, T. Kasper, "A Detailed Chemical Kinetic Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames",
Proc. Combust. Inst., 2008, 32, in press.
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Proc. Combust. Inst., 2008, 32, in press.
3. N. Hansen, J. A. Miller, T. Kasper, K. Kohse-Höinghaus, P. R. Westmoreland, J. Wang, T. A. Cool, "Benzene Formation in Premixed Fuel-Rich 1,3-Butadiene Flames", Proc. Combust. Inst., 2008, 32, in press.
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- 5 J. Wang, U. Struckmeier, B. Yang, T. A. Cool, P. Oßwald, K. Kohse-Höinghaus, T. Kasper, N. Hansen, P.R. Westmoreland, "Isomer-specific influences on the composition of reaction intermediates in dimethyl ether/propene and ethanol/propene flames", J. Phys. Chem. A, 2008, ASAP Article, 10.1021/jp8011188.
- 6 N. Hansen, S. J. Klippenstein, P. R. Westmoreland, T. Kasper, K. Kohse-Höinghaus, J. Wang, T. A. Cool, "A Combined ab-initio and Photoionization Mass Spectrometric Study of Polyynes in Fuel-Rich Flames", Phys. Chem. Chem. Phys., 2008, 10(3), 366-374.
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Number of Papers published in peer-reviewed journals: 23.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

C. A. Taatjes and T. A. Cool, "A Combustion Surprise", Science Highlight, ALS web site, August, 2005.

C. A. Taatjes, T. A. Cool, and J. A. Miller, "Combustion Chemistry at the ALS" Science Feature Article, 2005 ALS Activity Report.

T. A. Cool, Flame Chemistry Studies at the ALS, Science Highlight, ARO Chemical Sciences Division, 2005.

Number of Papers published in non peer-reviewed journals: 3.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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(d) Manuscripts

1. J. Wang, M. Chaos, B. Yang, T. A. Cool, F. L. Dryer, T. Kasper, N. Hansen, Patrick Oßwald, K. Kohse-Höinghaus, P. R. Westmoreland, "Composition of reaction intermediates for stoichiometric and fuel-rich dimethyl ether flames: Flame-sampling mass spectrometry and modeling studies", Physical Chemistry Chemical Physics, submitted.

2. T. Kasper, P. Oßwald, U. Struckmeier, K. Kohse-Höinghaus, C. A. Taatjes, J. Wang, T. A. Cool, M. E. Law, A. Morel, P.R. Westmoreland, "Combustion chemistry of the propanol isomers—investigated by electron ionization and VUV-photoionization molecular-beam mass spectrometry", Combustion and Flame, submitted.

Number of Manuscripts: 2.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Hubert Nguyen	0.10
FTE Equivalent:	0.10
Total Number:	1

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Bin Yang	0.50
Juan Wang	0.50
FTE Equivalent:	1.00
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Terrill A. Cool	0.10	No
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Hubert Nguyen, "Photoionization Mass Sp

Total Number:

1

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

1. RESEARCH OBJECTIVES

This research addresses perceived needs of the U.S. Army, first in the development and use of biodiesel fuels, and second in the combustion chemistry of small cyclic nitramines. Studies were completed of the chemistry of several simple methyl and ethyl esters chosen as surrogates for the long chain mono-alkyl esters that are primary constituents of biodiesel fuels. We have also completed measurements of the mole fraction profiles for reaction intermediates for morpholine, a heterocyclic nitramine, containing both ether and secondary amine functions. The simple structure of morpholine leads to a kinetic model that reveals mechanisms in common with the chemistry of nitrate ester propellants.

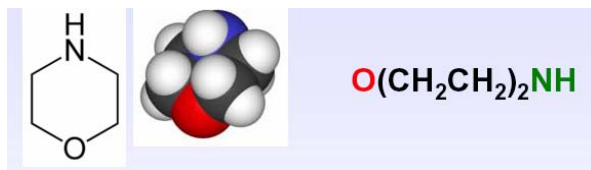
We have studied the flame chemistry of oxygenated fuels and fuel additives (dimethyl ether, ethanol, alkyl esters) proposed as clean burning alternatives to conventional liquid hydrocarbon fuels derived from petroleum. These studies respond to an urgent need to (1): define the key chemical reaction mechanisms responsible for observed reductions in polycyclic aromatic hydrocarbons, particulate matter, unburned hydrocarbons, and carbon monoxide when oxygenated fuels are used as replacements for conventional fuels and (2): understand the chemistry leading to potential increases in the emissions of other regulated hazardous air pollutants including aldehydes (formaldehyde, acetaldehyde) and ketones (acetone) inherent in the use of oxygenated fuels.

Molecular-beam synchrotron photoionization mass spectrometry and electron-ionization mass spectrometry are used for measurements of species mole fraction profiles for low-pressure premixed flames of oxygenated fuels and fuel mixtures. The fuels studied are: dimethyl ether (DME), ethanol, propene/DME, propene/ethanol mixed fuels, and 12 methyl and ethyl esters (methyl and ethyl formate, methyl and ethyl acetate, methyl and ethyl propanoate, methyl and ethyl propenoate, methyl methacrylate, methyl butanoate, methyl isobutanoate, and methyl crotonate) chosen as model compounds for studies of biodiesel combustion.

2. SUMMARY OF MOST SIGNIFICANT RESULTS

2.1 Studies of Nitrogenous Fuels Related to Propellant Chemistry

We have completed measurements of the mole fraction profiles for reaction intermediates for morpholine, a heterocyclic 6-membered fuel with the chemical structure:



which contains both ether and secondary amine functions. We have chosen morpholine for study because its simple cyclic structure lends itself to the development of a detailed

model of its flame chemistry. Although morpholine is somewhat distantly related to the nitrate ester components of propellant formulations, it is expected that common reaction mechanisms may exist for both classes of compounds. The nitrate esters are not appropriate for studies in low pressure flames at the ALS because of serious safety concerns.

Several dozen reaction intermediates have been observed at the ALS in low-pressure (30 Torr) flat laminar flames fueled with morpholine. Many of these are structural isomers that can, in many cases, be identified with flame-sampling molecular-beam photoionization mass spectrometry using tunable synchrotron radiation. Unambiguous isomeric identifications of many reaction intermediates require high level quantum calculations. These measurements lead to a postulated detailed fuel decomposition scheme in agreement with observations [1]. They also provide a basis to identify relevant nitrogen-containing targets for studies of thermodynamic and kinetic properties, which are crucially needed in the development of combustion mechanisms.

Although the morpholine flame shows a low tendency to form C₃-species as precursors to aromatics under the investigated slightly fuel-rich $\Phi=1.3$ (C/O=0.41) conditions, prominent combustion intermediates include CH₂O, NH₃, NO, HCN and HNCO. These substances are intermediates in the combustion of RDX and HMX and are likely to appear in most fuels with N-functions and therefore need to be considered in practical applications including DeNO_x processes [2].

2.2 Studies of Dimethyl Ether Flames

Molecular-beam synchrotron photoionization mass spectrometry and electron-ionization mass spectrometry are used for measurements of species mole fraction profiles for low-pressure premixed dimethyl ether (DME) flames with equivalence ratios ranging from near-stoichiometric conditions ($\Phi=0.93$) to fuel-rich flames near the limits of flat-flame stability ($\Phi=1.86$) [3]. The results are compared with predictions of a recently modified kinetic model for DME combustion [Zhao et al., *Int. J. Chem. Kinetics*, 2008, **40**, 1-18] that has been extensively tested against laminar flame speed measurements, jet-stirred reactor experiments, pyrolysis and oxidation experiments in flow reactors, species measurements for burner-stabilized flames and ignition delay measurements in shock tubes. The present comprehensive measurements of the composition of reaction intermediates over a broad range of equivalence ratios considerably extends the range of the previous experiments used for validation of this model and allows for an accurate determination of contributions of individual reactions to the formation or destruction of any given flame species. The excellent agreement between measurements and predictions found for all major and most intermediate species over the entire range of equivalence ratios provides a uniquely sensitive test of details of the kinetic model. The dependence on equivalence ratio of the characteristic reaction paths in DME flames is examined within the framework of reaction path analyses.

2.3 Studies of Mixed Hydrocarbon and Oxygenated Hydrocarbon Fuels

This work [4] provides experimental evidence on how the molecular compositions of fuel-rich low-pressure premixed flames are influenced as the oxygenates dimethyl ether (DME) or ethanol are incrementally blended to propene fuel (a representative hydrocarbon). Ten different flames with a carbon-to-oxygen ratio of 0.5, ranging from 100% propene ($\phi = 1.5$) to 100% oxygenated fuel ($\phi = 2.0$), are analyzed with flame-sampling molecular-beam mass spectrometry employing electron- or photoionization [4]. Absolute mole fraction profiles for flame species with masses ranging from $m/z = 2$ (H_2) to $m/z = 80$ (C_6H_8) are analyzed with particular emphasis on the formation of harmful emissions. Fuel-specific destruction pathways, likely to be initiated by hydrogen abstraction, appear to lead to benzene from propene combustion and to formaldehyde and acetaldehyde through DME and ethanol combustion, respectively. Figure 1 shows that while the concentration of acetaldehyde increases ten-fold as propene is substituted by ethanol, it decreases as propene is replaced with DME. In contrast, the formaldehyde concentration rises only slightly with ethanol replacement but increases markedly with addition of DME. Allyl and propargyl radicals, the dominant precursors for benzene formation, are likely to be produced directly from propene decomposition or via allene and propyne. Benzene formation through propargyl radicals formed via unsaturated C_2 intermediates in the decomposition of DME and ethanol is negligibly small. As a consequence, DME and ethanol addition lead to similar reductions of the benzene concentration, as illustrated in Fig. 2.

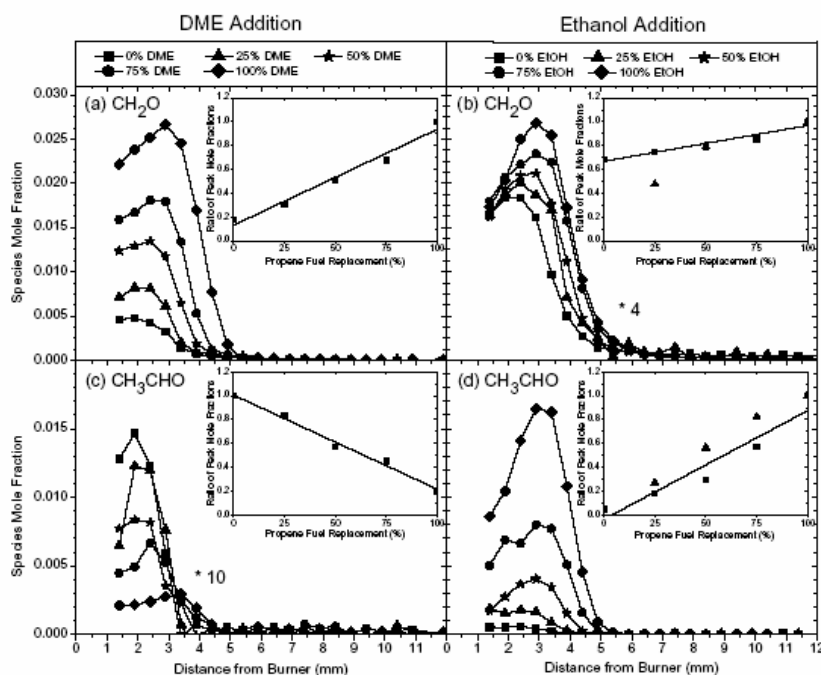


Figure 1: Formaldehyde and acetaldehyde mole fraction profiles for DME/propene and ethanol/propene fuel mixtures. To facilitate comparison, all mole fractions are multiplied by a factor of 4 in Fig. 1(b) and by a factor of 10 in Fig. 1(c).

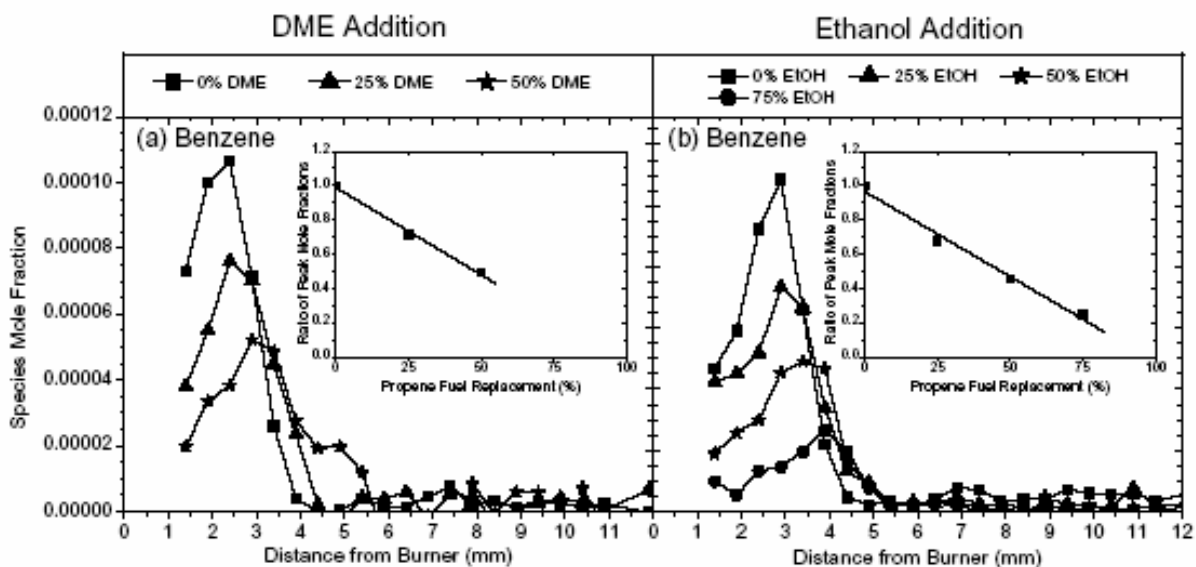


Figure 2: Benzene mole fraction profiles for DME/propene and ethanol/propene fuel mixtures. No measurable contributions to C_6H_6 formation from the presence of either oxygenated additive are observed.

2.4 Modeling of Biodiesel Combustion with Flame Studies of Selected Methyl and Ethyl Esters

Extensive studies of diesel engine emissions for both neat biodiesel fuels and for blends of oxygenated additives with petroleum diesel show pronounced fuel-specific trends in the composition of emitted pollutants. In an effort to describe the reaction pathways responsible for these observed effects, we are studying the influences of fuel structure on the composition of reaction intermediates in the combustion of 12 selected methyl and ethyl ester surrogates for biodiesel fuels:

- methyl and ethyl formate
- methyl and ethyl acetate
- methyl and ethyl propanoate
- methyl and ethyl propenoate
- methyl methacrylate
- methyl butanoate
- methyl isobutanoate
- methyl crotonate

The broad objective of this work [5,6] is to define the reaction pathways that account for fuel-specific differences in the production of aldehydes, ketones, CO, prompt CO_2 , and the unsaturated hydrocarbon precursors to PAH and soot.

These 12 fuels have been selected using three different criteria intended to identify fuel-specific effects on the flame chemistry [5,6]. First, comparison of the flames of structural isomers allows detailed analysis of the influence of functional

groups on the fuel consumption pathways. Second, these fuels are chosen to reveal fuel-specific influences of methoxy vs ethoxy ester functions (cf. Fig. 4) and degree of unsaturation and chain branching (cf. Fig. 5). The isomeric esters under study are shown in Fig. 3. Similar overall combustion characteristics (e.g., temperature profiles, equivalence ratios, C/O ratios, and major species composition) are often achievable for isomeric fuels, which assists quantitative analysis of flame chemistry. Differences in initial fuel destruction reactions and comparisons of the composition of reaction intermediates highlight the influences of fuel structure on the kinetic mechanism.

Isomeric Fuels

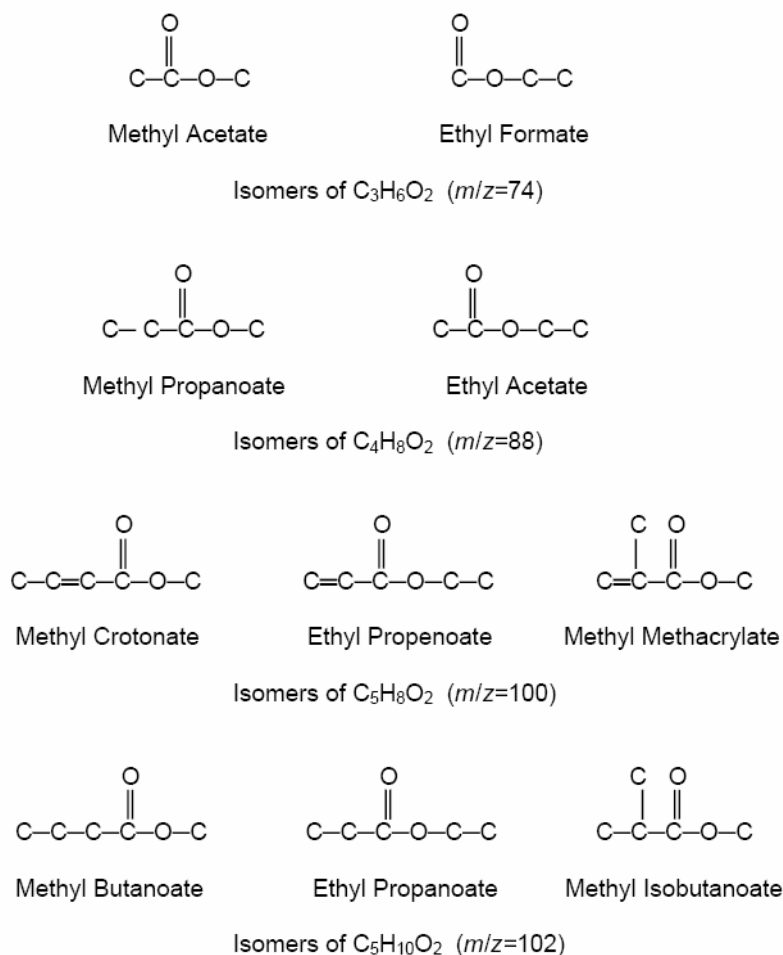


Figure 3: Structural Isomers

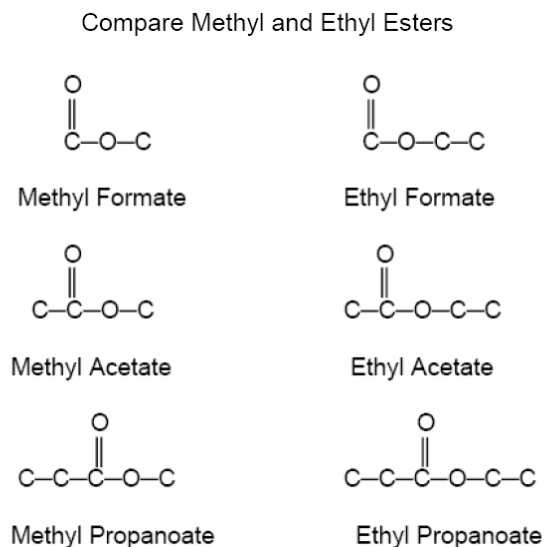


Figure 4: Fuels selected for studies of the fuel-specific influences of the (methoxy vs ethoxy) ester functions

Study Influences of Fuel Structure for Biodiesel Surrogates

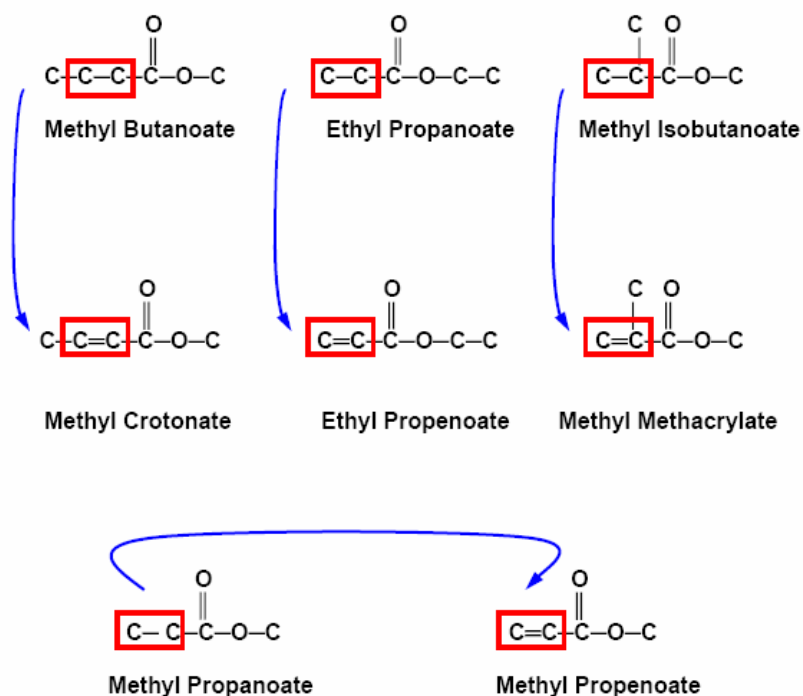


Figure 5: Fuels selected to examine the influences of the degree of unsaturation and chain branching on the composition of reaction intermediates

A detailed chemical kinetic reaction mechanism has been developed for a group of four small alkyl ester fuels, consisting of methyl formate, methyl acetate, ethyl formate and ethyl acetate [6]. This mechanism is validated by comparisons between computed results and recently measured intermediate species mole fractions in fuel-rich, low pressure, premixed laminar flames. The model development employs a principle of similarity of functional groups in constraining the H atom abstraction and unimolecular decomposition reactions for each of these fuels. As a result, the reaction mechanism and formalism for mechanism development are suitable for extension to larger oxygenated hydrocarbon fuels, together with an improved kinetic understanding of the structure and chemical kinetics of alkyl ester fuels that can be extended to biodiesel fuels. Variations in concentrations of intermediate species levels in these flames are traced to differences in the molecular structure of the fuel molecule.

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6. C. K. Westbrook, W. J. Pitz, P. R. Westmoreland, F. L. Dryer, M. Chaos, P. Oßwald, K. Kohse-Höinghaus, T. A. Cool, J. Wang, B. Yang, N. Hansen, T. Kasper, "A Detailed Chemical Kinetic Mechanism for Oxidation of Four Small Alkyl Esters in Laminar Premixed Flames", *Proc. Combust. Inst.*, **32** (2008), in press.